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Trace-Level Determination of Specific VOCs (Volatile Organic Compounds) in Whole-Air Samples in the Presence of High-Level Contamination

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INTRODUCTION

The analysis of whole-air samples for selected trace-level, volatile organic compounds (VOCs) can be complicated by the presence of other nontargeted compounds that constitute an interference to quantitation. For instance, in an industrial environment the presence of hydrocarbons and various solvents may mask the ppbv-level concentration of targeted VOCs. This is particularly true for analytical systems that rely upon nonspecific detectors (FID, PID) or separation techniques with inadequate resolution. In the work reported here, a series of six samples was prepared in which a group of 41 nonpolar VOCs were diluted to the 2-4 ppbv level in a variety of air mixtures, some of which included high levels of contamination. Table 1 lists these sample matrices and the approximate contamination levels.

EXPERIMENTAL METHODS

Equipment

Analytical equipment consists of two fully automated gas chromatographic instruments. Both systems include a Hewlett Packard 5880 Level 4 GC equipped with a Nutech 320-01 (modified) sample preconcentrator (McClenny *et al.* 1984). System 1 employs a wide bore OV-1 type capillary column (531-µm i.d., 30-m length) and is equipped with parallel flame ionization and electron capture detectors (FID, ECD, respectively). No provision is made to remove water from the sample stream. System 2 employs a high-resolution OV-1 type capillary column (310- µm i.d., 50-m length) and is equipped with a Hewlett-Packard 5970 MSD, a quadrupole mass selective detector. For this system, it is necessary to predry the analytical sample with a Nafion tube, permeable-membrane dryer (Pleil and Oliver 1985, McClenny *et al.* 1984). Use of these dryers discriminates against polar compounds.

The sample format consisted of pressurized whole air in 6-L volume SUMMA®-polished canisters; the canisters were purchased from Demaray Scientific Instruments, Pullman, WA. A stainless-steel diaphragm pump (Biospherics, Hillsboro, OR) was used to pressurize canisters with sample gas.

Procedure

A known dynamic dilution mixture of 41 VOCs of interest and three polar compounds was prepared in humid zero air at the 8- to 12-ppbv level per compound. During real-time analysis of this mixture, six evacuated canisters were filled to positive pressure. Each canister was then analyzed to assure that the concentrations were as expected. Each canister was bled to ambient pressure and sealed. Dilutions to 30 psig were then performed with the stainless steel diaphragm pump using various matrix gases as listed in Table 1, which resulted in at least 2- to 4-ppbv concentrations for each of the 41 VOCs.

The six samples were then each analyzed by system 1 (FID and ECD). A 500-cc volume of each sample was cryogenically preconcentrated prior to analysis. This analysis indicated the complexity of the sample (see Figure 1) and yielded quantitative estimates on the high-level contamination in some samples (see Table 1). Each sample was then analyzed by system 2 in the selected ion monitoring (SIM) mode. A sample volume of 250 cc was analyzed by monitoring three ions per compound. This method discriminates against all but the compounds of interest, unless a contaminant compound appears with the same column retention time and

similar ionic fragments. This run was used to determine if a compound could be detected and, if so, to quantify the amount present.

RESULTS AND DISCUSSION

The qualitative results of the analyses are presented in Figure 1, where the FID chromatograms and the total ion chromatograms for the MSD-SIM are shown. As expected, a broad spectrum detector like the FID quickly loses the ability to determine trace level compounds in the presence of contaminants. Though somewhat more specific, even the total ion chromatograms show the effects of high-level contamination. This occurs because even very minor fragments of a high-concentration contaminant may become important.

However, when both fragmentation pattern and retention times are used to qualify results, useful information can be extracted. An automated, calibrated program was applied to each MSD-SIM data file. The "base peak" (most abundant) ion was extracted for quantitation, and two other ions were used to confirm identification (these computer-generated results are listed in Table 2). Though the large contaminants interfered with some of the ions, the identification scheme, including a restriction of ± 0.1 minutes retention time and ± 15% to ± 25% tolerance on the relative abundance of the two secondary ions, often allowed extraction of quantitative data. In some instances quantification was not correct with the current method. These values are annotated in Table 2. Apparent problems were correctable or explainable in some cases.

When concentrations were reported in excess of the expected level, contributions from the dilution gas are likely, but, at least in the case of allyl chloride, a coeluting compound with a similar fragmentation pattern contributed to the reported concentration. Where concentrations were much lower than expected, particularly in the extremely contaminated sample 6, retention time window tolerances were exceeded for benzene and toluene so that post-processing of data was necessary to calculate the values shown in Table 2. Various chlorinated species were also reported too low for sample 6, and, to a limited extent, for samples 4 and 5. The source of error was not evident in these cases. Finally, the overall bias of sample 4 with respect to sample 1 is probably due to the uncertainty in the dilution process.

CONCLUSIONS

A SIM mass spectrometric analysis using the Hewlett-Packard mass selective detector as a GC detector generally gave quantitative results for specific trace-level compounds even in the presence of a very complex and/or highly concentrated mixture of contaminants. In some cases, such as in the detection of allyl chloride, the problem of quantitation could perhaps be solved by suitable alteration of the system software. In other cases, further study is required to determine appropriate remedial measures.

REFERENCES

1. **McClenny, W.A., J.D. Pleil, M.W. Holdren, and R.N. Smith.** 1984. Automated cryogenic preconcentration and gas chromatographic analysis of volatile organic compounds in air. *Anal. Chem.* 56:2947.

2. **Pleil, J.D. and K.D. Oliver.** 1985. Evaluation of various configurations of Nafion dryers: Water removal from air samples prior to gas chromatographic analysis. TN-85-03. Research Triangle Park, NC: Northrop Services Inc. – Environmental Sciences.

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TRACE-LEVEL DETERMINATION OF SPECIFIC VOCs IN WHOLE-AIR SAMPLES IN THE PRESENCE OF HIGH-LEVEL CONTAMINATION. J. D. Pleil, K. D. Oliver, Northrop Services, Inc. – Environmental Sciences, Research Triangle Park, NC 27709, and W. A. McClenny, Environmental Monitoring Systems Laboratory, Environmental Protection Agency, Research Triangle Park, NC 27711

Selected target compounds in a whole-air matrix were determined at the ppbv level in the presence of high concentration contamination. Known samples of 41 nonpolar volatile organic compounds (VOCs) were prepared and then diluted to approximately 2- to 4-ppbv each. The dilution gas for the different samples was ambient air spiked with either solvent vapors, gasoline vapors, natural gas, or automobile exhaust. Zero air and "clean" ambient air were also used as dilution gases for comparison. Adequacy of the procedure to extract quantitative information for the 41 nonpolar target VOCs is discussed.

TABLE 1. DESCRIPTION OF THE DILUTION AIR MATRICES. EACH SAMPLE ALSO CONTAINED 41 VOCs OF INTEREST AT 2- to 4-ppbv LEVELS

Sample	Dilution Air Composition	Contamination Levels[a] (Approx.)
1	Zero air - dry	None
2	Outdoor ambient air (Clear, sunny, windy day)	No appreciable contamination
3	Natural gas in ambient air	~6000 ppbv methane[b] ~90 ppbv ethane[b] ~15 ppbv propane Plus ~ 30 hydrocarbons (1 to 10 ppbv)
4	Solvents: 1-propanol, 2-propanol, methanol, ethanol, ethyl acetate, acetonitrile, and acetone in ambient air	Ranging from 500 to 3000 ppbv
5	Outdoor ambient air with automobile exhaust; sampled within 30 cm of exhaust pipe of running car	More than 150 peaks at 1 to 60 ppbv
6	Gasoline vapors in ambient air	More than 150 peaks at 100 to 10,000 ppbv

[a]Approximate measurements – quantitation from FID, identification confirmed by MS scan.

[b]Based on propane quantitation.

TABLE 2. GC-MSD RESULTS (ppbv) FROM SELECTED ION MONITORING FOR THE 41 VOCs OF INTEREST. SAMPLES WERE PREPARED BY DILUTION AS INDICATED IN TABLE 1.

Compound	Sample 1 Zero Air	Sample 2 Outdoor Ambient Air	Sample 3 Natural Gas	Sample 4 Polar Solvents Vapor	Sample 5 Auto Exhaust	Sample 6 Gasoline Vapor
Dichlorodifluoromethane (Freon 12)	3.62	3.42	4.42	4.41	3.21	1.82 [a]
Chloromethane	2.82	2.97	3.64	3.45	3.00	2.65
1,1-Dichloro-1,2,2,2-tetrafluoroethane (Freon 114)	3.46	3.21	5.20	5.53	2.86	4.12
Chloroethylene (vinyl chloride)	2.49	2.63	3.08	3.01	2.83	78.7 [a]
Bromomethane	4.10	3.81	4.77	4.26	4.62	3.42
Chloroethane	3.81	3.98	4.82	5.29	3.41	1.11 [a]
Trichlorofluoromethane (Freon 11)	4.21	4.18	6.25	5.48	3.59	4.77
1,1-Dichloroethylene (vinylidene chloride)	2.24	2.16	2.58	2.35	1.78	1.50 [a]
Dichloromethane	3.72	3.72	159. [b]	150. [b]	3.37	128. [b]
3-Chloropropylene (allyl chloride)	3.87	3.39	5.03	1.68 [a]	16.0 [c]	5665 [c]
1,1,2-Trichloro-1,2,2-trifluoroethane	2.00	2.16	2.64	2.05	1.77	1.72
1,1-Dichloroethane	3.65	3.71	4.30	4.14	3.01	3.40
cis-1,2-Dichloroethylene	3.94	3.55	4.41	3.93	3.14	2.33 [a]
Chloroform	2.05	1.88	2.41	2.24	1.63	1.11 [a]
1,2-Dichloroethane	2.61	2.58	3.06	2.69	2.29	6.06 [a]
1,1,1-Trichloroethane (methyl chloroform)	2.18	2.21	3.43	3.95	1.85	1.66
Benzene	3.08	3.08	4.68	5.91	3.84	597.
Carbon tetrachloride	2.26	2.30	2.76	2.36	1.96	1.62
1,2-Dichloropropane	3.78	3.47	4.35	4.38	2.96	3.34
Trichloroethylene	2.32	2.36	2.74	2.34	2.01	1.73
cis-1,3-Dichloropropene	1.16	1.06	1.36	1.15	0.92	0.12 [a]
trans-1,3-Dichloropropene	1.05	0.91	1.21	1.05	0.91	0.21 [a]
1,1,2-Trichloroethane	3.57	2.84	4.16	2.71	2.66	6.28 [a]
Toluene	2.93	3.07	4.77	4.02	50.5	1724.
1,2-Dibromoethane (EDB)	1.86	1.83	2.17	1.99	1.66	1.74
Tetrachloroethylene	2.37	2.33	2.71	2.20	2.05	1.68
Chlorobenzene	2.06	2.09	2.58	2.13	1.84	2.25
Ethylbenzene	3.46	3.23	4.19	3.80	1.39	122
m,p-Xylene	7.10	6.72	8.85	8.13	40.1	407.
Styrene	3.33	3.47	4.18	4.02	13.3	4.60
1,1,2,2-Tetrachloroethane	3.63	3.50	4.32	3.82	2.87	1.44 [a]
o-Xylene	3.54	3.34	4.37	4.09	18.6	168
4-Ethyltoluene	3.38	3.29	4.32	4.59	11.2	88.0
1,3,5-Trimethylbenzene	3.40	3.16	4.17	4.13	11.6	47.0
1,2,4-Trimethylbenzene	3.44	3.32	4.48	5.17	33.9	143.
m-Dichlorobenzene	3.56	3.68	4.22	3.55	3.28	3.49
Benzyl chloride	2.58	2.64	3.23	2.67	2.59	2.15
p-Dichlorobenzene	3.26	3.46	4.02	3.32	3.04	3.30
o-Dichlorobenzene	3.43	3.63	4.20	3.48	3.21	3.24
1,2,4-Trichlorobenzene	4.07	3.72	4.89	4.05	4.19	4.17
Hexachlorobutadiene	2.68	2.54	3.26	2.67	2.28	2.27

[a]Unresolved problem.

[b]Unexpectedly high value; however, identification confirmed by MS scan.

[c]Coeluting interferant with similar ion pattern.

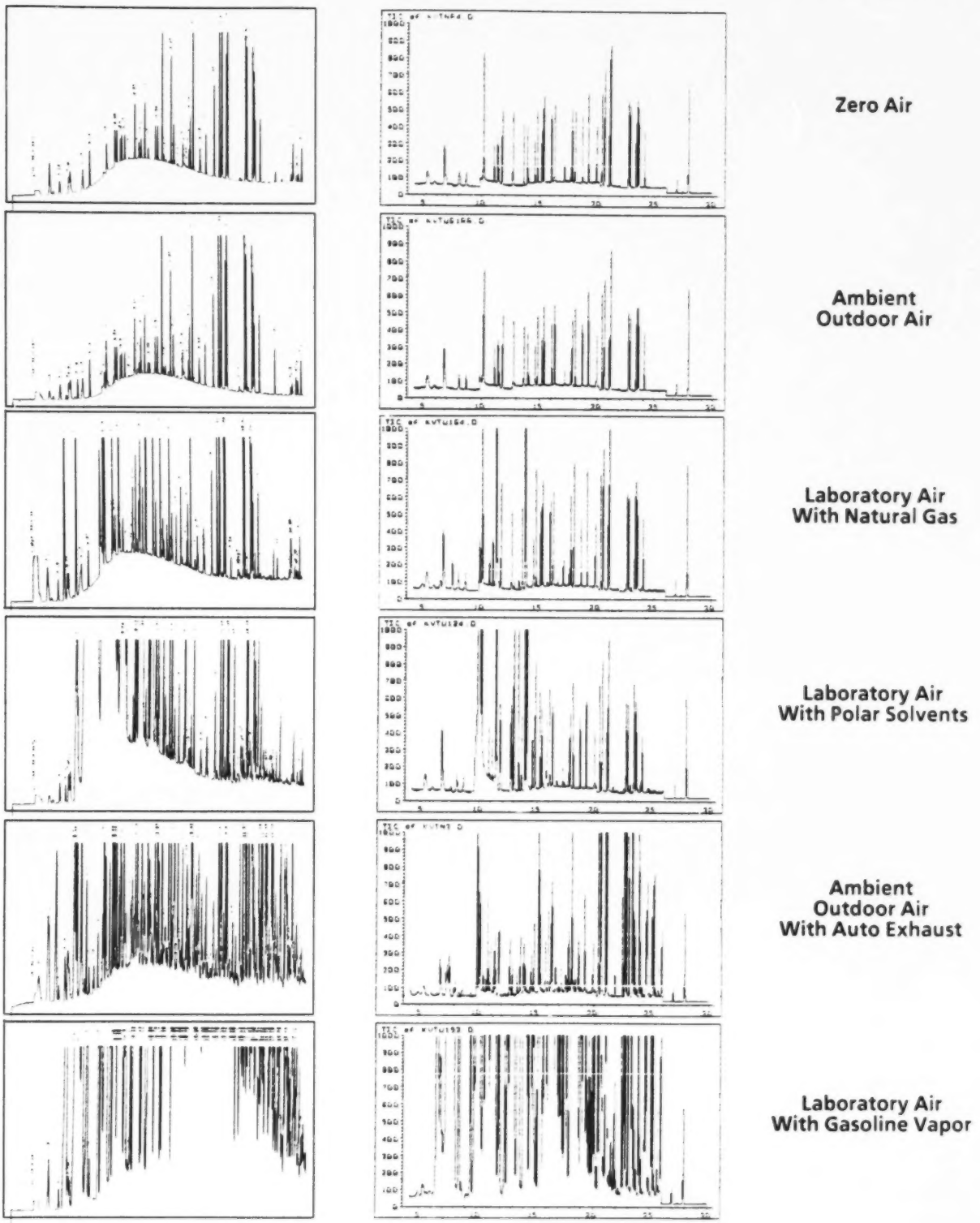

Figure 1. Comparisons of FID and MSD-SIM Chromatograms for Various Samples.